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I. A Study of the Hydrogen Electrode, of the Calomel Electrode and of Contact Potential.
II. A Study of the Ethylene Electrode.
III. Studies in Oxidation and Reduction.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
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I. A STUDY OF THE HYDROGEN ELECTRODE, OF THE CALOMEL ELECTRODE AND OF CONTACT POTENTIAL.

I. INTRODUCTION

The increasingly accurate results which have been obtained by various workers who have studied the constancy, reproducibility, and, especially, the applicability of the hydrogen electrode and of the calomel electrode, made the continued study of these systems seem well worth while. With the idea of continuing the work on this subject that was begun in Acree's laboratory by Desha,[1] and continued by Loomis,[2] and Myers[3] with very interesting results, this investigation was undertaken.

The work of Hildebrand[4] in his study of the application of the hydrogen electrode as an instrument for determining the titration curves for various acids, bases and salts, that of Schmidt and Finger[5] in their study of the "Potential of a Hydrogen Electrode in Acid and Alkaline Solutions," and that of Bjerrum[6] in connection with his work on the "Elimination of Contact Potentials" show a few of the important phases of this work along inorganic lines. The hydrogen electrode was used by Denham[7] in measuring the degree of hydrolysis of several inorganic salts, and of aniline hydrochloride.

The chief object of the study of the hydrogen electrode in this laboratory has been to devise a method for allowing us to investigate a number of such catalytic reactions as the following:

---

[1] Desha: Diss., Johns Hopkins Univ., 1909; Am. Chem. Jour., 46, 638 (1911).

[2] Loomis: Ibid., 1911; Am. Chem. Jour., 46, 585–622 (1911).

[3] Am. Chem. Jour., 50, 396 (1913).

[4] Jour. Am. Chem. Soc., 35, 847–871 (1913).

[5] Jour. Phys. Chem., 12, 406–416 (1908).

[6] Zeit. Elektrochemie, 17, 389–393 (1911).

[7] Jour. Chem. Soc., 93, 41 (1908).

$$CH_3CONH_2 + \overset{+}{H}\overset{-}{Cl} \rightleftharpoons CH_3CON\overset{+}{H}_3 + \overset{-}{Cl} \rightleftharpoons$$

$$CH_3CONH_3Cl + H_2O \rightleftharpoons CH_3COOH + \overset{+}{NH_4} + \overset{-}{Cl}$$

It is at once apparent that there are so many unknowns in this reaction that the conductivity and reaction velocity methods together cannot allow us to determine whether the cation or nonionized salt or both are hydrolyzed, but if we could measure at any moment the concentration of the hydrogen ions by means of the hydrogen electrode, we could solve this problem. Conductivity measurements by Nirdlinger showed that there can be at most only a few percent of the amide salt and it is therefore necessary to develop the hydrogen electrode to a high degree of reproducibility, if it is to be of service in this connection.

As an illustration we can choose a solution in which five percent of the hydrogen ions combine with the amide to form the amide salts. In order to show a change of 0.1 percent in the hydrogen ion concentration and hence 2 percent in the concentration of the amide salt, we must make the measurements accurate to 0.000025 volt. Now it is highly desirable in such studies to know the concentration of the amide salts to within 0.1 percent, and hence we must be able to measure e. m. f. with an accuracy of 0.000001 volt. The smaller the percent of hydrogen ions disappearing in such salt-formation, the greater the accuracy demanded in the e. m. f. measurement. We have tried to devise methods to allow us to approach a reproducibility of 0.000001 volt. In studying the hydrogen electrode, the calomel electrode has been used as a standard; consequently the latter needed to be studied with respect to its constancy and ease of reproduction. This involves five lines of study, which, briefly, are:

I. The determination of the average value of the potential of a large number of electrodes, arranged in batteries of ten, which were made up very carefully from chemicals purified by the best known methods, while the apparatus was kept as clean as practicable.

II. The best methods for preparing and keeping the hydrogen electrodes in condition for immediate use.

III. Intercomparisons of different electrodes and systems.

IV. Modifications of the apparatus, especially with reference to the heating system, the bath, new forms of apparatus for calomel electrodes,[1] and new hydrogen electrode apparatus.

V. Measurement of the systems

(*a*) H_2–Pt–0.1 N HCl–0.1 N KCl–HgCl–Hg.
(*b*) 0.1 N KCl–HgCl–Hg.
(*c*) 0.1 N HCl–HgCl–Hg.
(*d*) Hg–HgCl–0.1 N HCl–0.1 N KCl–HgCl–Hg.
(*e*) H_2–Pt–0.1 N HCl.
(*f*) H_2–Pt–0.1 N HCl–0.1 N HCl–HgCl–Hg.
(*g*) Hg–HgCl–0.1 N HCl sand filling 0.1 N KCl–HgCl–Hg.

II. HISTORICAL

Loomis gave a brief summary of the previous work in the study of calomel and hydrogen electrodes in which he stated that Ostwald[2] was the first to describe the normal calomel electrode, which he found reproducible to within one millivolt and to have the potential $+0.5600 + 0.0006 (t^\circ - 18^\circ)$ as determined by the drop-electrode method by Rothmund.[3] The study of Coggeshall[4] on the constancy of calomel electrodes; that of Smale[5] on gas elements, in which he showed that the electromotive force of the cell is independent of the material in the electrode, if not acted upon chemically; and that of Wilsmore,[6] Richards,[7] Gewecke,[8] Saure,[9] and others are discussed briefly by Loomis, besides which he gives an extensive bibliography.[1] Wilsmore[2] tabulated the results of the studies of Smale, Neumann, and himself. He found for the potential of the normal calomel electrode the mean value 0.283 volt which was based on his adoption as a zero of potential that of the hydrogen electrode towards a solution normal with respect to hydrogen ions. The elements studied by these workers and from which this result was calculated, included the following systems:

---

[1] These newest forms are not closed by constricting and sealing the glass at the top as were those designed by Myers and Acree (Am. Chem. Jour., **50**, 398, footnote), nor are the ground-glass tops used by Loomis employed. The top of each single electrode has a ground-glass stopper, and a glass cover tube is placed over this and fits down on a small bulb blown in the upper tube of the electrode, to which bulb the cover tube is attached hermetically with sealing wax. A full description appears later in this dissertation.

[2] Ostwald-Luther: "Physiko-chemische Messungen," 3rd Edition, p. 441.

[3] Zeit. phys. Chem., **15**, 15 (1894).

[4] Ibid., **17**, 62 (1895).

[5] Ibid., **14**, 577 (1894).

[6] Ibid., **35**, 296 (1900); **40**, 385 (1902).

[7] Ibid., **24**, 39 (1897).

[8] Ibid., **45**, 685 (1903).

[9] Ibid., **47**, 146 (1904).

(*a*) H_2–Pt–1 *N* HCl–1 *N* HCl–HgCl–Hg
(*b*) H_2–Pt–1 *N* HCl–1 *N* KCl–HgCl–Hg
(*c*) H_2–Pt–1 *N* HCl–0.5 *N* KCl–0.5 *N* KCl–HgCl–Hg
(*d*) H_2–Pt–1 *N* H_2SO_4–1 *N* KCl–HgCl–Hg
(*e*) H_2–Pt–1 *N* H_2SO_4–0.5 *N* KCl–HgCl–Hg

Special mention should be made in this brief historical survey, of the work of Schoch,[3] Sauer,[4] Salm,[5] Planck,[6] Palmaer,[7] Nernst,[8] Lorenz and Mohn,[9] Lewis and Sergeant,[10] Abegg and Cummings,[11] and particularly that of Bjerrum.[12]

III. THEORETICAL

The potential of the hydrogen electrode toward the solution in which it is immersed is dependent upon the pressure of the hydrogen gas and upon the osmotic pressure of the hydrogen ions in the solution, as was shown by Nernst.

The theory regarding the calculation of the electromotive force between a calomel electrode and a hydrogen electrode is explained by Loomis, as follows:

---

[1] Loomis: p. 55, Diss., Johns Hopkins University, 1911.
[2] Zeit. phys. Chem., 35, 296 (1900).
[3] Jour. Phys. Chem., 14, 665 (1910).
[4] Zeit. phys. Chem., 47, 146 (1904).
[5] Zeit. Elektrochemie, 10, 341 (1904).
[6] Wied. Ann., 40, 561 (1890).
[7] Zeit. phys. Chem., 59, 129 (1909).
[8] Ibid., 56, 544 (1906).
[9] Ibid., 60, 422 (1907).
[10] Jour. Am. Chem. Soc., 31, 363 (1909).
[11] Zeit. Elektrochemie, 13, 17 (1907).
[12] Ibid., 17, 58 (1911).

"In the comparison of a calomel electrode against a hydrogen electrode in a solution whose hydrogen ion concentration is $H^{\cdot}$, we find that if π represents the observed electromotive force, π_1 the potential of the calomel electrode against a hydrogen electrode when immersed in a solution with unit concentration of hydrogen ions, F the quantity of electricity necessary to deposit one gram ion of hydrogen and π_2 the contact potential between the solutions of the system, then the equation $\pi = \pi_1 - \frac{RT}{F} \log_e H^{\cdot} + \pi_2$ holds when the hydrogen gas is under atmospheric pressure. From this equation when $T = (25^{\circ} + 273^{\circ})$ we find that

$$\log_{10} H^{\cdot} = -\frac{\pi - \pi_1 - \pi_2}{0.0591}.$$

"The value of π is obtained by actual measurement with the potentiometer, π_1 is calculated from some system in which π_2 and $\frac{RT}{F} \log_{10} H^{\cdot}$ are known and π has been previously measured, and π_2 is calculated. The best system for determining the value of π_1 is: H_2–Pt/0.1 *N* HCl/0.1 *N* KCl/HgCl–Hg in which π can be measured, $\frac{RT}{F} \log_e H^{\cdot} = 0.0591 \times \log_{10} 0.0922$ and π_2 can be calculated by some such formula as that of Planck."

The calculation of π_2 is difficult and methods have been sought for eliminating this contact potential between the two systems. For this purpose there has been interposed between the two solutions in question a saturated solution of a very soluble salt, whose anions and cations have nearly equal migration velocities. Abegg and Cumming[1] used for this purpose ammonium nitrate. Denham assumed they were correct in claiming that the use of ammonium nitrate practically eliminates contact potential. He used it in measuring the hydrolysis of aniline hydrochloride. Desha and Loomis showed that it does not entirely eliminate contact potential.

The sand-filling method of Bjerrum for eliminating contact potential is much more efficient, as shown by Myers. The apparatus required for it consists of a Peligot tube filled with very pure sand to within an inch and a half of the top of each branch. The one side is tightly stoppered and 0.1 N KCl is poured in very cautiously and allowed to soak through thoroughly until it reaches the center line of the small bulb at the bottom of the tube. A siphon carrying a stopcock and filled with 0.1 N KCl is now fitted tightly by means of a ground joint into the side of the Peligot tube, which has been soaked with the potassium chloride solution. The stopper is removed from the other side and 0.1 N HCl is introduced with care, so that the hydrochloric acid and potassium chloride solutions come in contact in a sharp line in the middle of the lowest bulb of the Peligot tube. A siphon of 0.1 N HCl is attached in the manner described above to the hydrochloric acid side. When a hydrogen electrode battery is to be connected to a 0.1 N KCl calomel battery for intercomparison, the siphon of potassium chloride is introduced into the calomel battery and the siphon of hydrochloric acid is connected with the hydrogen electrode battery. In case the calomel battery is made up with 0.1 N HCl for an electrolyte and sand-filling device is not necessary; the hydrogen battery can be connected directly to the calomel battery, as illustrated at J, in Fig. 1.

---

[1] Zeit. Elektrochemie, 13, 17 (1907).

IV. EXPERIMENTAL

1. Apparatus

The use of the potentiometer for measuring electromotive force; of the Weston cells as primary standards; of an oil bath for maintaining constant temperature, the oil eliminating electrical leakage currents far better than water; and of the electrodes themselves, is in the main the same as that described by Loomis with the exception of such modifications and additions as are described below.

There are now in use five Weston standard cells loaned by the Bureau of Standards. The use of the potentiometer and Weston cells as arranged at present permits an accuracy of within 0.00001 volt.

The temperature regulation is correct to within 0.01°, the experiments being carried out at 25°. A specially designed milk-scale thermometer is used. It is made of Jena 59 III glass and consists of a 2 cc bulb and a capillary tube having small bulbs between the fixed points 0°, 5°, 10°, 15°, 20°, 25°, 30° and 35°. On each side of the fixed points the milk scale is graduated in 0.02° over a range of 0.2°. By the use of a specially arranged cathetometer we can easily read the thermometer to 0.0005°. The bulb wall was made rather thicker than usual in order to diminish the errors usually incident to Beckmann thermometers having thin walls. By having the bulbs in the capillary the length of the thermometer is reduced to $16^1/_2$ inches. This type has proved to be very reliable, the observed temperatures being reproducible to within 0.003° at 25° and 0.005° at 35°.

In place of the electric bulb used by Loomis for heating there has been introduced a heating coil consisting of nichrome wire wound in a spiral upon insulated posts, and divided by lead wires into three sections. The heating capacity of each section is equivalent to that of a 32 candle power light. These sections may be thrown in series or parallel by means of a switch board. It is found that *better regulation of temperature* and electromotive force is obtained by their use for the reason that the coils are exposed directly to the oil and retain the heat for a shorter time than does a lamp.

The thermo-regulation is accomplished by means of the toluene regulator and the master relay system, first devised in Acree's laboratory for maintaining a given temperature constant to within a few thousandths of a degree. In the master-relay system, the toluene thermo-regulator and a two-volt storage circuit actuate a 250 ohm Bunnell relay, or a very sensitive No. 18 Weston relay, which, in turn, operates several other relays acting as short-circuits for the current for the heating coil. Each spark gap is short-circuited by a condenser and a high resistance lamp to prevent sparking or arcing.

The stirring of the oil is accomplished by a fan stirrer which drives the oil down over the heating coil whence it passes under a glass plate supported four inches above the bottom of the bath; the oil flows to the further end of the bath and returns after passing with good contact through the gridiron toluene thermo-regulator, above the glass plate which supports the apparatus; it is during the last stage of the trip that it comes in contact thoroughly with the apparatus. During the passage of the oil under the glass plate the oil passes over pipes through which cold water is circulated when the external temperature renders it desirable. By means of this system the regulation was constant to within 0.01°.

The stirrer (*C*) circulating the oil is attached to the shaft A in Fig. 1, which also carries, above the surface of the oil, the fan (*B*) for stirring the air. A closely fitting top of wood and glass covers the entire bath. The shaft carries the friction wheel (*D*) which, with the shaft and fans, is revolved rapidly by means of the small friction wheel (*E*) attached to the shaft of the motor. The motor (*F*) is supported just outside the end of the bath by an iron frame work (*G*) which is bolted, through holes in supporting brass plates, to the table on which the bath rests. This arrangement avoids vibrations great enough to interfere appreciably with reading the galvanometer

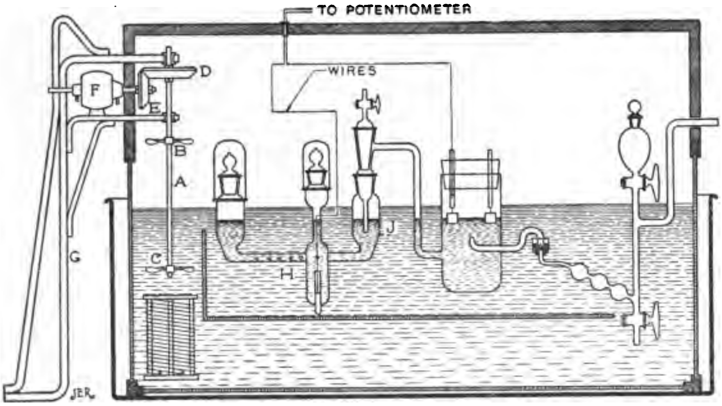

Fig. 1

on the wall at the farther end of the room. *This system avoids the troubles incident to the apparatus used by Loomis, such as the breaking and slipping off of belts, bad vibration and the open bath.*

The galvanometer is supported on a marble slab which is cemented in the wall so as to avoid as far as possible the effect of jarring caused by machinery elsewhere in the building.

The cover consists of a frame work of glass and wood which is held in position over the bath by strips of brass which project for several inches along the outside of the bath at the four corners. It has a top which is as long as the bath and is hinged to the main frame of the cover about four inches from the top back edge. This top consists of two parts hinged together in such a way that it will readily fold back upon itself and permit free access to the interior of the bath. At the end of the bath at which the motor for stirring is located, there are arranged two sliding doors which have had such sections cut from them as will permit the passage of the shaft of the motor. The doors close around this shaft and thus exclude the exterior air. The other end has a hole cut through it for the passage of the glass tube which connects the palladium asbestos tube of the hydrogen purifying apparatus to the hydrogen wash apparatus described by Loomis. Through the top, toward the back, there are three holes for the admission respectively, of the wires used in connecting the cells with the potentiometer, of the wiring for an electric lamp for heating the air when necessary to about 26°, and of the thermometer held by a stopper. *The purpose of the lamp referred to is to heat the air enclosed by the cover to about 26° and thus prevent the condensation, in the upper parts of the calomel electrodes, of the water vapor above the solutions of potassium chloride* and avoid changes in the concentrations and electromotive forces. The air-fan referred to serves to circulate the air and prevent superheating above any one battery. An ordinary thermometer is considered sufficiently accurate for this air space, and no thermo-regulator is necessary as the lamp is not used when the room is warm enough to heat the air of the bath sufficiently to interfere with the regulation of the heating of the oil. The lamp used is blackened with a heavy coating of lamp black and shellac so as to prevent radiation.

For the study of a calomel battery over a period of several years the form used by Myers and Acree is well adapted. It differs from the form used by Loomis in that the upper tubes of the single electrodes are constricted and sealed instead of being closed by means of ground-glass caps containing stopcocks. To study a battery for a short time and to empty and refill seemed highly desirable. *To do this with the form used by Myers and Acree it would be necessary after two or three fillings to seal a new top to each electrode; as such a process incurs considerable risk of breaking an expensive piece of apparatus, it was thought best to modify the form in such a way that it could be used repeatedly without this danger and at the same time without permitting the leaking in of oil as did the form used by Loomis. With this idea in mind the form (H) illustrated in Fig. 1 was devised.* The essential differences consist in the use of ground-glass stoppers for closing each electrode and in using sealing-wax to fasten the glass caps down upon the bulbs shown in Fig. 1. This form of battery and that used by Myers and Acree contain much wider tubes connecting the single electrodes than were used by Loomis. *This decreases the electrical resistance and also permits more rapid diffusion and attainment of equilibrium.*

Several modifications of the hydrogen apparatus used by Loomis are described by Myers and Acree. The use of *pure gum* stoppers, of the device for preventing the hydrogen electrodes from drying while in storage during the summer, and of the short-circuiting "crow-foot" are important changes which they introduced. The storage apparatus for the hydrogen electrodes is illustrated in Fig. 2 and Fig. 3. An ordinary crystallizing dish, A, about half filled with 0.1 *N* HCl is placed in a desiccator, F, which contains enough 0.1 *N* HCl to rise to about $^1/_4$ of the height of the crystallizing dish. The tube D, passing through a stoppered hole, 5, in the side

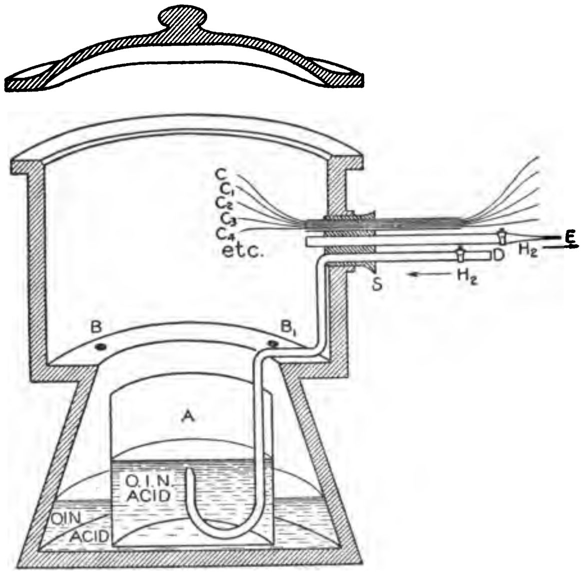
C
C_1
C_2
C_3
C_4
etc.
E
H_2
D
S
H_2
B
B_1
A
O.I.N.
ACID
OIN
ACID

Fig. 2

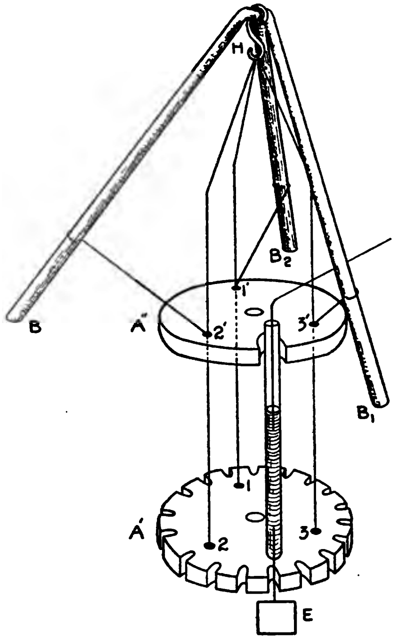
H
B_2
B
A''
1'
2'
3'
B_1
1
A'
2
3
E

Fig. 3

of the desiccator, and so bent as to have an outlet under the surface of the acid in the crystallizing dish, serves as an inlet for hydrogen gas, while the tube E serves for its escape. Fig. 3 shows the framework which supports the electrodes so that they are about half submerged in the acid in the crystallizing dish. B, B_1 and B_2 are the three legs of a glass tripod, upon which, by means of the hook H, and the supporting gold wires 1′–1, 2′–2, 3′–3, are hung the circular glass disks A′ and A″. These disks have cut into their edges indentations suitable for holding the electrodes, as illustrated by E; after the set of electrodes has been placed in position in the disks a gold wire is bound around them in such a way that they will not slip if handled with ordinary care. The tripod is now placed in the desiccator so that the feet rest upon the shoulder B and B_1 in Fig. 2. When the electrodes are not in use, and yet it is desired to keep them active, the wires C, C_1, C_2, C_3, etc., are short-circuited in a cup of mercury outside the desiccator. Inside the desiccator each of these wires is introduced into a different capillary tube carrying a hydrogen electrode. When it is wished to intercompare the hydrogen electrodes, the wires are removed from the cup of mercury; the wire leading to any one electrode (which serves as a standard) is connected by means of a cup of mercury and wiring to the potentiometer; the other wires are similarly, one at a time, connected to the potentiometer and the intercomparison of the potentials of the electrodes is made. Table VI shows that the deviation among a number of electrodes stored in this way for eleven months was generally less than 0.0001 volt. This is highly satisfactory as electrodes left dry even three months vary from 0.0001 volt to 0.06 volt, and cannot be used at all without replatinization.

The barometer is a *Fuess* normal and carries verniers for correcting for capillarity.

The connection between the hydrogen electrode and the calomel is made by means of the sand-filling device of Bjerrum as described later.

With regard to the calomel electrode a little change in the preparation and introduction of the material has been made from the methods used by Loomis. In the preparation of the calomel the precipitation of the mercurous chloride is effected at present by the addition of a dilute solution of potassium chloride to the solution of mercurous nitrate. The form of calomel battery has been modified as described.

Some of this work is concerned with the study of batteries which were made up by Dr. Myers. Two of them designated as B–IV and B–V were made up in May, 1912, while B–II was made up May 1, 1913. The former two have not been refilled during this time and have had a history worth considering at length. Table I shows the data for battery B–IV—0.1 *N* KCl–HgCl–Hg, part of which has been presented by Myers and Acree.

The notations "with wires," "without wires," etc., refer to the readings below; the notations "with wires" means that the crow-foot short-circuit device was in use. "Without wires" means it was not in use. The notation "readings made while storage cell was connected to charging switch" means that wires from the storage cell were connected to the switch leading to the charging current. Although the switch was open there was a leak sufficient to affect the galvanometer, as the readings show. "Changed short-circuit to wood cups" means that in place of the "crow-foot" there was introduced a set of wood cups containing mercury; these were connected by wires to the capillaries in the batteries. The cups of mercury were now short-circuited with one another by means of a frame of brass. "Changed short-circuit to glass cups" means that glass cups of mercury were used in place of wood, it being found that the wood cracked and let the mercury escape. On the whole the figures show that the best system is the "crow-foot" used by Myers and Acree.

Table II shows the data battery B–V — 0.1 *N* KCl–HgCl–Hg; some of the readings were made before this present study was begun. The notes and notations explain some of the variations in the readings.

TABLE 1—BATTERY B-IV, 0.1 *N* KCl–HgCl–Hg

Prepared May 2, 1912

The first values recorded were obtained 18 hours after preparation

(Values expressed in millionths of a volt)

Electrode 1 used as standard

Date	2	3	4	5	6	7	8	9	10
With wires									
1912									
May 3	140	41	10	38	26	50	25	55	180
May 4	11	5	12	8	8	80	35	2	4
May 6	15	4	6	11	4	7	2	9	5
May 7	12	7	10	13	2	30	12	15	11
May 9	1	9	9	11	10	16	10	10	30
Without wires									
May 11	50	60	15	70	60	90	45	80	75
With wires									
May 22	8	9	3	7	7	10	1	9	10
1913									
Apr. 11	8	7	6	7	7	7	8	8	5
Readings made while storage cell was connected to charging switch									
Nov. 4	14	24	2	16	24	46	56	56	46
Storage cell disconnected									
Nov. 14	23	2	8	10	6	8	28	1	9
Nov. 20	5	9	9	4	2	14	10	9	4
Changed short-circuit to wood cups									
Dec. 14	16	59	23	20	5	10	11	0	3
Dec. 22	2	11	23	14	14	34	51	26	32
1914									
Feb. 9	29	54	52	59	73	73	61	61	61[1]
Feb. 23	19	1	2	2	34	16	16	26	17
Mar. 2	7	25	11	—[2]	13	8	8	14	14
Mar. 7	2	10	24	12	2	6	2	5	5
Mar. 22	9	9	6	8	15	9	11	20	20
Wire crow-foot replaced									
May 7	3	27	35	33	5	18	—[3]	2	16
May 15	2	27	50	43	23	32	27	29	19

---

[1] Bath had been out of use for a long time. Equilibrium had not been attained when these readings were made.

[2] The wire leading to capillary had broken off from No. 5.

[3] The wire leading into capillary of electrode No. 8 was not amalgamated and did not make contact.

TABLE II—BATTERY B-V, 0.1 *N* KCl-HgCl-Hg

Prepared May 2, 1912
First readings recorded 18 hours after preparation
(Values expressed in millionths of a volt)
Electrode 1 used as standard
With wires

Date	2	3	4	5	6	7	8	9	10
1912									
May 3	21	16	28	54	35	142	45	25	15
May 6	4	5	2	5	9	10	1	3	7
May 22[1]	4	2	4	5	1	55	56	15	5
Oct. 17	5	6	8	12	4	9	0	7	2
Oct. 22	1	9	0	7	4	2	5	7	6
Nov. 4	5	0	1	7	9	5	8	5	4
1913									
Jan. 7	2	6	2	4	3	2	3	2	4
Jan. 14	0	0	2	4	2	6	1	4	0
Apr. 11	8	7	6	7	7	7	8	8	5
May 5	0	2	0	1	1	1	1	2	4
Nov. 4[2]	97	82	87	81	96	64	26	20	45
Nov. 5[3]	8	20	4	21	22	3	21	13	38
Nov. 12	0	2	17	2	8	11	34	3	4
Nov. 20	7	0	5	16	16	2	10	8	2
Nov. 25	2	2	2	18	16	16	2	8	2
Dec. 14	5	8	2	2	10	2	7	6	6
1914									
Feb. 11	0	4	0	8	2	3	22	4	0
Feb. 20	2	4	2	2	2	0	15	2	3
Mar. 2	3	3	0	2	2	4	16	6	9
Mar. 17	0	2	0	7	4	3	9	4	3
Mar. 22	1	2	3	3	5	0	5	1	4
May 8[4]	42	63	58	55	58	67	82	67	68

An examination of the values shown in Tables I and II shows that within four days from the time of preparation of the calomel batteries, the potentials of the electrodes will differ among themselves by not more than 20 millionths of a volt. The values found in the cases in which the crow-foot short-circuiting was maintained show that this system tends to bring about a closer agreement of the electrodes than is obtained when there is no short-circuiting. The close agreement between the electrodes at the end of two years shows the constancy of the system.

---

[1] Battery had been used in making measurements, solution was disturbed.

[2] Readings made while storage cell was connected to charging switch, short-circuiting arrangement was bad.

[3] Better short-circuiting.

[4] Battery had been used to make intercomparisons. Solutions were disturbed.

TABLE III (*a*)—COMPARISON OF BATTERIES B–IV AND B–V, 0.1 *N*
KCl–HgCl–Hg B–IV against Cell I B–V
after 18 months B–IV B–V

Cell	Without wires	Same date without wires	With wires
1	0.000005	0.000028	0.000001
2	0.000032	0.000031	0.000009
3	0.000029	0.000017	0.000000
4	0.000021	0.000025	0.000007
5	0.000025	0.000012	0.000004
6	0.000012	0.000022	0.000002
7	0.000023	0.000031	0.000005
8	0.000038	0.000014	0.000007
9	0.000010	0.000027	0.000006
10	0.000024	—	—

TABLE III (*b*)—COMPARISON OF BATTERIES B–IV AND B–V, 0.1 *N*
KCl–HgCl–Hg B–V against Cell I
of B–IV B–IV against Cell I of B–V

Cell		
1	0.000009	0.000001
2	0.000012	0.000007
3	0.000000	0.000004
4	0.000007	0.000002
5	0.000009	0.000000
6	0.000001	0.000001
7	0.000008	0.000000
8	0.000004	0.000001
9	0.000005	0.000000
10	0.000006	0.000003

TABLE IV—BATTERY No. VI, 0.1 *N* KCl–HgCl–Hg

(Values expressed in millionths of a volt)
Electrode 1 used as standard
With wooden cups of mercury

Date	2	3	4	5	6	7	8	9	10
1914									
Feb. 9	43	45	45	118	89	31	31	6	79
Feb. 11	2	46	47	127	94	52	60	56	97
Unblackened 32 c. p. lamp in air space over bath near electrodes 1, 2, 3, 4 and 5 of battery Without wires since Feb. 12th									
Feb. 18	162	181	183	284	276	258	303	293	346
With wooden cups of mercury									
Feb. 23	83	5	108	176	113	127	136	121	157
Mar. 2	108	94	126	182	108	157	180	160	192
Blackened 8 c. p. lamp in air space									
Mar. 17	85	95	95	105	90	85	90	82	71
Mar. 22	95	117	96	109	109	99	110	106	115
With wires									
May 1	11	50	36	29	0	35	35	23	36
May 8	14	30	25	23	30	25	17	12	18

TABLE V—BATTERY No. VII, 0.1 *N* KCl–HgCl–Hg

(Values expressed in millionths of a volt)
Electrode 1 used as standard
With wires

Date	2	3	4	5	6	7	8	9	10
1914									
Feb. 9	2	36	48	70	104	26	7	2	52
Feb. 11	15	20	32	45	77	20	2	2	37
Feb. 13	25	2	6	38	43	10	28	23	54
Unblackened 32 c. p. light placed in air space above bath									
Feb. 18	7	19	35	45	33	31	5	11	17
Feb. 20	5	17	44	55	44	23	14	14	13
Feb. 23	25	28	38	54	51	19	14	8	23
Mar. 2	14	42	38	52	34	1	8	18	2
Blackened 8 c. p. light in air space									
Mar. 8	5	32	28	32	29	33	12	4	13
Mar. 22	6	1	25	30	33	7	11	9	2
May 1	29	12	14	14	22	51	32	0	20
May 8	18	21	15	5	9	35	9	6	31

Table III (*a*) and Table III (*b*) show the comparison of the electrodes of one battery against a single electrode of another. It should be noted that the effect of the use and non-use of the short-circuiting system is marked. The values shown in Table III (*b*) were obtained after the short-circuiting system had been in use for some time immediately previous.

Tables IV and V give the history of Batteries B–VI and B–VII. These batteries are the latest form, *i. e.*, they have ground-glass stoppers for each electrode and protecting glass covers. The values shown are not so good as those found for batteries B–IV and B–V, but this is due to better technique in preparing the materials for B–IV and B–V. So far as the form of battery is concerned, there seems no reason to believe the forms used for B–IV and B–V are either more or less preferable than those used for B–VII, for producing constancy and reproducibility of the electrodes. It is interesting to note the effect of the use of the unblackened 32 c. p. light and of blackened (to diminish radiation) 8 c. p. light for heating the air-space enclosed by the glass and wood top above the bath. Attention is directed to the fact that in the case of B–VII the crow-foot was used throughout its history, while for B–VI wooden cups of mercury were used. The results in the case of B–VII are rather better than for B–VI. This is believed to be due to the difference in the method of making the reading. In the case of B–VI the readings were made through the cups of mercury, each of which was connected, by means of a screw soldered to a wire, to an electrode. The soldering of the wire to the screw is believed to have brought about resistance differences which affected the readings on the potentiometer considerably. It will be noted that the crow-foot system was made use of in the case of B–VI previous to the last two sets of readings and that the values of the potentials of the different electrodes approached a more constant value.

Table VI shows the history of a set of hydrogen electrodes. Some of the values shown were obtained previous to the time this present study was begun. Whenever the

TABLE VI—H_2-Pt-0.1 *N* HCl. STOPPER I

Electrodes were placed in 0.1 *N* HCl after being left in box three months. H_2 allowed to run about five hours before first record was taken. Electrode 10 chosen as standard (Values in millionths of a volt)

Date	9	8	7	6	5	4	3	2	1
1912									
Jan. 18	186	820	470	700	62930	956	58810	155	2558
Jan. 19	232	178	168	169	4988	1736	3445	696	820
Jan. 20	175	81	101	195	2654	895	1720	405	525
Electrodes replatinized and treated as described									
Jan. 22	50	75	227	30	636	218	430	97	73
Began use of "Crow-foot," replatinized and electrolyzed									
Jan. 24	15	35	53	40	98	31	15	15	47
Jan. 26	6	10	10	10	46	9	5	25	13
Jan. 27	7	3	0	5	10	6	0	40	2
Jan. 31	10	6	6	3	28	6	6	37	4
Rubber dissolving in acid as shown below									
Feb. 1	42	25	46	14	46	58	44	78	44
Apparatus cleaned. Electrodes and stoppers boiled in distilled water									
Feb. 4	11	15	12	6	10	18	12	25	25
Feb. 6	4	4	1	3	3	8	2	2	5
Stove in bath burned out and temperature drops 6 degrees									
Feb. 9	6	3	3	5	4	2	6	6	1
Without wires									
Feb. 17	25	10	15	15	14	12	9	15	—[1]
Feb. 19	20	3	15	15	26	26	25	34	27
Rubber dissolving in acid									
Mar. 6	50	60	130	55	115	90	50	140	56
Electrodes boiled in distilled water and placed in constant pressure desiccator									
1913									
June 1	20	3	5	2	3	1	1	3	0
Apr. 25	5	3	6	6	7	5	4	1	3
Electrodes stored in desiccator until March 29, 1914, then placed in 0.1 *N* HCl and exposed to stream of H_2									
1914									
Mar. 31	24	20	33	192	105	46	44	70	11
Electrodes replatinized. Placed in bath May 6									
May 8	9	20	12	6	8	25	9	12	25

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[1] This electrode was broken and repaired, giving results shown on next date.

TABLE VII—Hg–HgCl–0.1 *N* KCl–0.1 *N* HCl–Pt–H_2
(Bar. in Atms., 1.010; Cor. in e. m. f., —0.00023)

	0.427341		
	0.427342		
	0.427336		
	0.427342		
	0.427335		
	0.427342		
	0.427340		
	0.427335		
	0.427338	Other similar averages	
	0.427340		0.427106 (*a*)
			0.427109 (*b*)
Av.	0.427339		0.427109 (*c*)
Bar. Cor.	0.00023		0.427108 (*d*)
Av.	0.427109	Av.	0.427108
Cor. av.	0.426919	Cor. av.	0.426918

electrodes were replatinized they were boiled with distilled water for several hours after the replatinization.

Table VII shows a comparison of a fresh calomel battery and a hydrogen battery without use of a device for eliminating contact potential. These values were obtained by Myers and are reported here for the sake of comparison with a system in which there was used for elimination of contact potential a saturated KCl solution. The values (*a*), (*b*), (*c*), (*d*) are averages of sets of values obtained at other times. All readings shown were made before the Fuess normal barometer was obtained, and the "Cor. Av." notation means that the readings of the old barometer were not correct, hence the values noted "Av." need the correction applied.

TABLE VIII
0.1 *N* KCl–HgCl–Hg sat. KCl 0.1 *N* HCl–Pt–H_2
B–V–Bar. in atms., 0.990–Bar. Cor. = 0.00026

0.39971	0.39981	Av.	0.39974
0.39972	0.39976	Bar. cor.	0.00026
0.39980	0.39971		
0.39974	0.39972		0.40000
0.39972	0.39973	Cor. av.	0.39982

Table VIII shows the values obtained when saturated KCl is used to eliminate contact potential. The values obtained agree closely with those of Bjerrum.

The results for the system 0.1 *N* HCl–HgCl–Hg were about the same as those obtained by Myers and Acree.

Summary

1. The object of this investigation has been to devise better methods and apparatus for the accurate measurement of the electromotive force of hydrogen and calomel electrodes. Chief among the improvements in apparatus were (1) a new heating and stirring device for the oil bath which permits a more accurate regulation of temperature and electromotive force; (2) an air bath above the oil bath to heat the air and prevent evaporation from the liquids and changes in concentration and electromotive force; (3) a new form of calomel battery which can be filled, emptied and cleaned very quickly and easily without danger of breakage and which gives as accurate values as those used by Myers; (4) a storage reservoir in which hydrogen electrodes can be kept active in hydrochloric acid in an atmosphere of hydrogen and kept constant in electromotive force to within 0.0001 volt. The preparation of very pure calomel by the use of potassium chloride and the use of weight methods in lieu of volume methods for the preparation of the hydrochloric acid have increased the ease of making satisfactory solutions.

2. By the use of these improvements in the apparatus and methods it is possible to obtain much more easily than formerly a reproducibility of 0.01 millivolt with the hydrogen and calomel electrodes.

3. The 0.1 *N* KCl–HgCl–Hg system seems to be constant and reproducible to within 0.01 millivolt. In addition it is a comparatively stable system.

4. The hydrogen electrode has proven to be an easily reproducible and constant system, extremely sensitive to small amounts of impurity, thus indicating its rapidity and accuracy for determining small hydrogen ion concentrations,

which would render it very valuable in determining the hydrogen ion concentration in cases of catalysis by acids.

5. It is found that the system Hg–HgCl–0.1 *N* KCl–0.1 *N* HCl–Pt–H_2 is an extremely accurate and constant element. It undoubtedly gives one of the best intercomparisons that can be obtained.

6. The 0.1 *N* HCl–HgCl–Hg system is found to be rather unsatisfactory over long periods of time. The intercomparison of the individual electrodes indicate that its constancy continues over only a short period of time, due to the formation of $HgCl_2$ and Hg, with a possible further decomposition. The values obtained during the past year support the evidence previously found in this laboratory.

7. An accuracy of 0.01 millivolt was obtained when the following precautions were observed:

a. The materials were most carefully purified. The mercury was purified by washing about five hundred times with three percent nitric acid. It was rinsed with water and let stand under concentrated sulfuric acid. It was distilled three times in a current of air. This was used for making calomel and in the calomel electrode.

The calomel was made by dissolving mercury, purified as indicated, in *N*/5 nitric acid and using an excess of mercury. To the solution of mercurous nitrate a solution of thrice recrystallized potassium chloride was added. The calomel was shaken out with water repeatedly and filtered and washed to get rid of nitric acid and potassium nitrate. It was then shaken with approximately *N*/10 potassium chloride to get rid of the excess of water. Finally it was saturated with carefully standardized *N*/10 potassium chloride prepared from the ignited recrystallized potassium chloride.

The *N*/10 potassium chloride was prepared from potassium chloride recrystallized three times and ignited to constant weight. Conductivity water was used in making up the solution.

The *N*/10 hydrochloric acid was made from redistilled hydrochloric acid. The hydrogen was prepared by electrolysis of dilute sodium hydroxide, using nickel electrodes. The hydrogen was passed through a palladium asbestos tube and a washing apparatus containing $N/10$ hydrochloric acid.

b. A temperature regulation in the oil to within 0.01° was maintained for at least two days previous to making readings. The temperature above the bath was roughly kept at 26° simply to prevent the condensation of liquid in the upper part of the apparatus which protruded above the oil.

c. When not in use for several weeks the hydrogen electrodes were stored in the container illustrated in Figs. 2 and 3. They were kept saturated with $N/10$ hydrochloric acid and hydrogen.

d. The hydrogen was bubbled through the $N/10$ hydrochloric acid against the electrodes. It was believed that this is more efficient than simply maintaining an atmosphere of hydrogen above the hydrochloric acid.

e. The individual electrodes of the calomel (and hydrogen) batteries were short-circuited together by means of the wire crow-foot. This produced and maintained a very close agreement.

II. A STUDY OF THE ETHLYENE ELECTRODE

I. Introduction

The constancy and reproducibility of the hydrogen electrode and calomel battery having been shown to be sufficiently accurate, it has seemed advisable to extend its application to other series of measurements even though it has been necessary to study these cases somewhat qualitatively. These studies have been termed qualitative for the reason that many improvements in methods and apparatus will be necessary before accurate results can be obtained. The hydrolysis of aniline hydrochloride, as carried out by Denham,[1] by Desha,[2] and by Loomis,[3] gave values quite satisfactory as compared with the calculated values. In a case of this kind we have a solution of varying composition and increasing complexity. The hydrogen electrode has proved to be very accurate, direct, and rapid in such cases.

Let us examine the hydrolysis of an amide in the presence of hydrochloric acid:

$$RCONH_2 + HCl + \overset{+}{H} + \overset{-}{Cl} + RCONH_3Cl + RCON\overset{+}{H}_3 + \overset{-}{Cl} + H_2O \longrightarrow RCOOH + \overset{+}{NH}_4 + \overset{-}{Cl}, \text{ etc.}$$

After a moment's consideration it is seen that there is no method (*e. g.*, conductivity method) of determining the concentrations of all the constituents of such a system for the reason that too many unknown factors are present. The application to this case of the hydrogen electrode, which furnishes a measure of the hydrogen (hydroxide) ion concentrations would be of great help; the method is best seen in simple organic substances like aniline hydrochloride. This substance is selected for the reason that considerable data obtained by other methods are at hand and agree sufficiently well when the formula

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[1] Jour. Chem. Soc., 93, 41 (1908).

[2] Diss. Johns Hopkins Univ., 1909.

[3] Ibid., 1911.

$$\frac{K_w}{K_b} = \frac{[C_{H^+}]^2 \times \text{volume}}{\left[1 - \frac{\text{Percent hydrolysis}}{100}\right] \times \text{ionization}}$$

is used for calculating this relationship. The reader's attention is called to the work of Loomis, Denham, Desha and Bredig in this connection.

Other cases of applicability are: the hydrolysis of cane sugar,

$$C_{12}H_{22}O_{11} + HOH \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6;$$

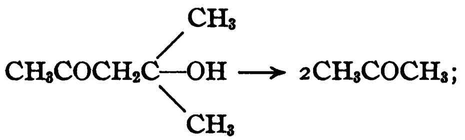
ester and amide catalysis,

$$CH_3COOCH_3 + H_2O = CH_3COOH + CH_3OH$$
$$CH_3CONH_2 + H_2O = CH_3COONH_4;$$

breaking down of diazoacetic ester into glycolic acid ester and nitrogen,

$$N_2CHCOOC_2H_5 + H_2O \longrightarrow (OH)H_2CCOOC_2H_5 + N_2;$$

the change of diacetone alcohol into acetone,



$$CH_3COCH_2C(CH_3)_2{-}OH \longrightarrow 2CH_3COCH_3;$$

and especially cases in which the compounds are weakly dissociated. In cases of this last type the conductivity method presents extreme difficulties.

Ethylene Electrode

The most important investigation carried out under this topic of qualitative experiment consisted in the use of a new electrode which we have termed the ethylene electrode. This consists in the use of ethylene gas on one side and chlorine, hydrogen, oxygen, etc., gas on the other side of the system. Ethylene gas was prepared by the method of Gladstone and Tribe, in which ethylene bromide and copper-zinc couple were used. The copper-zinc couple was prepared by pouring a solution of copper sulphate over granulated zinc several times until a good coating of copper was obtained. Alcohol and ethylene bromide in the proportions 12 : 1 were used and to this mixture water was added to slight turbidity. The mixture was placed in a small balloon flask with a tight stopper and then the copper-zinc couple was added. The gas soon began to be evolved and it was passed through another flask completely surrounded by a freezing mixture in order to condense any ethylene bromide that might be carried along mechanically. The gas is then conducted through a solution of sodium hydroxide, potassium dichromate and water into a third cylinder containing dilute sulphuric acid. From this cylinder the gas is received in a gasometer by the displacement of water. Several liters of the gas were collected in this way and reserved for use in the electrode work. As far as it has been possible to gain any information from the literature nothing has been attempted with an electrode of this kind.

The apparatus necessary for experiments of this kind consists of two platinum electrodes of the same type as described in connection with the hydrogen electrode. In order to make a complete system it is necessary to use some known element whose electromotive force has carefully been worked out. In connection with this phase of the work, the chlorine element has been chosen and reference to the very important work of Lewis and his co-workers is made at this time. The electrolyte chosen for the system was 0.1 *N* hydrochloric acid, which was carefully standardized in this laboratory. This acid was first prepared by the method of Hulett, and then pycnometric measurements were made on the stock solution and these were supplemented by a great many quantitative determinations. A more complete description of this phase of the work will appear in a monograph on this subject. The container used for this study was essentially a U tube with a stopcock between the two halves of the apparatus. A diagram of this apparatus will likewise appear in the above-mentioned monograph.

Method of Experimentation

Emphasis is again laid upon clean apparatus and good chemicals even though the work is only qualitative in this particular case. About three hundred cubic centimeters of tenth normal hydrochloric acid was placed in the U tube. The stopcock between the two halves was closed and the apparatus was ready for the insertion of the electrodes. A three-hole gum stopper was used for each half of the apparatus. One hole was used for holding the electrode in place, the second for the inlet of gas, and the third for the exit of gas. The inlet tube extended below the level of the lower edge of the electrode and thus allowed the gas to bubble against the surfaces of the electrode. The exit tube was drawn to a capillary so that outside air was excluded. The entire apparatus was placed in a constant temperature bath and the gases allowed to flow into each side of the apparatus for fifteen or twenty minutes until saturation was nearly complete. The gas in each case was run through a wash solution of tenth normal hydrochloric acid. The wires leading to the potentiometer were adjusted and the system was in condition to make the ordinary electromotive force measurements. The following tables show the results of three different samples of ethylene:

TABLE I

C_2H_4–Pt–0.1 *N* HCl — 0.1 *N* HCl–Pt–Cl_2

Time	E. M. F.	Time	E. M. F.
12.15	0.850925	3.05[1]	0.741360
12.25	0.856430	3.10	0.723500
12.28	0.857228	3.20	0.714000
12.40	0.874720	3.30	0.708250
12.45	0.873475	3.40	0.704350
12.55	0.864720	3.45	0.696300
1.00	0.864750	3.55	0.693400
2.00	0.821220	4.00	0.691300
2.30	0.816920	4.05	0.688950[2]
2.35	0.817140	4.10	0.487500[3]
2.40	0.817650	4.20	0.874000
2.45	0.819940	4.30	0.747320[4]
2.50	0.824170	4.35	0.647300
2.55	0.823810	4.45	0.420000[5]
3.00	0.822880	5.00	0.448100

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[1] At this stage of the experiment oxygen and ethylene in equal volumes were allowed to flow in against the electrode.

[2] Ethylene stopped for five minutes.

[3] Oxygen stopped for ten minutes.

[4] Oxygen in equal proportions started.

[5] Oxygen in large excess.

TABLE II

C_2H_4–Pt–0.1 *N* HCl — 0.1 *N* HCl–Pt–Cl_2

Time	E. M. F.	Time	E. M. F.
2.35	0.901200	4.00	0.081000
2.40	0.902610	4.05	0.109200
2.45	0.914500	4.15	0.200000
2.47	0.917300	4.20	0.377000[2]
2.50	0.931400	4.25	0.457000
2.55	0.927500	4.30	0.459200
3.20	0.927600	4.40	0.571000
3.25	0.929500	4.45	0.749500
3.30	0.936000	4.50	0.929000
3.35	0.945600	4.55	0.931500
3.40	0.928000	5.00	0.928500
3.50	0.053700[1]	5.05	0.927500
3.55	0.044200		

TABLE III

C_2H_4–Pt–0.1 *N* HCl — 0.1 *N* HCl–Pt–Cl_2

Time	E. M. F.	Time	E. M. F.
10.35	0.887000	12.01	0.967450
10.55	0.923250	12.10	0.964600
11.00	0.951050	12.20	0.962700
11.10	0.961200	12.40	0.963600
11.30	0.943900	1.00	0.962500
11.55	0.964200	1.02	0.961500

The choice of chlorine as a part of this system was brought about by the fact that ethylene and chlorine combine readily and form ethylene chloride. It will be noticed that the initial electromotive force in all three experiments is approximately nine-tenths of a volt. The system remained fairly constant under uniform conditions. In order to find out if this observed E. M. F. was due to the presence of oxygen or hydrogen in the C_2H_4, oxygen was allowed to flow into the system in a volume equal to that of the ethylene and we noticed a dropping off of the potential, as we should expect. This case is observed in Table I, Note 1. The same table shows the rise and fall of the potential as the amounts of oxygen and ethylene are varied (Notes 2, 3, 4, 5).

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[1] The ethylene gas was entirely shut off and only oxygen allowed to flow in.

[2] Oxygen stopped entirely and only ethylene entering.

The same fact is more distinctly noted in the case of Table II, Note 1, where the E. M. F. becomes very small. It is noticed in this table that the E. M. F. increased as soon as the flow of oxygen was stopped and "pure" ethylene was allowed to bubble in, and that the system returned quite rapidly to its normal value. Table III shows an experiment in which ethylene is used against chlorine, and the E. M. F. remaining fairly constant at approximately 0.9625 volt. These experiments show apparently that ethylene gas when used in a gas electrode sets up an electromotive force of considerable amount and probably proceeds in a manner described below. As analysis of the ethylene showed that it is not absolutely pure, the next phase of our work will be to prepare the pure gas free from hydrogen, oxygen, ethane, etc., in order to prove beyond any question that pure ethylene gives the electrode described above.

The object of these studies is to learn whether ethylene combines with chlorine, bromine, hydrogen, etc., through an electronic transfer which can be used to develop an E. M. F.; as the preliminary study is certainly in harmony with this idea we may interpret the reaction as follows for the present:

$$CH_2 = CH_2 + Cl_2 \longrightarrow \overset{+}{C}H_2 - \overset{+}{C}H_2 + 2\overset{-}{Cl} \longrightarrow CH_2Cl-CH_2Cl$$

Summary

The work which has already been carried out on the study of the ethylene electrode indicates that it is an entirely new system; that it is a system possessing a very high electromotive force; that it is easily reproducible and constant as illustrated by the three separate tables submitted. Furthermore, it is apparent that chemically pure ethylene is difficult to prepare. Finally, the theory of its action as a gas electrode involves the idea that the ethylene loses two electrons to the electrode and then combines with the chloride ions.

III. STUDIES IN OXIDATION AND REDUCTION

The Electromotive Force of the Reaction $HCHO \xrightarrow{O} HCOOH$

Qualitative.—Many of the ordinary reactions which we observe each day serve as excellent examples for the study of electromotive force. The work of Acree and his co-workers leads the student of chemistry to regard the common reactions more carefully in accordance with the theory of ionic and molecular reactivity. The physical chemist should no longer believe that only ions participate in each reaction. The theory of Arrhenius and later workers taught us that the ions were the carriers of electrical charges and that it was their function to bring about chemical change. Accepting this view as a partial explanation and adding to this the newer conception of Acree in which the nonionized salts are regarded as an important factor in reactions, might we not suppose that the nonionized part carries a part of the electrical charge in an equilibrium phase such as:

$$NaOC_2H_5 + IC_2H_5 \longrightarrow \overset{+}{Na}OC_2H_5 + \overset{-}{I}C_2H_5 \longrightarrow$$
$$C_2H_5I.NaOC_2H_5 \text{ or } \overset{+}{C_2H_5} + INa\overset{-}{O}C_2H_5 \longrightarrow NaI + (C_2H_5)_2O$$

Without doubt electromotive force work will aid in studying these rapidly changing systems and complexes, and the accuracy and rapidity of this kind of method will greatly help the investigator to measure these values.

In making a study of this reaction, it is necessary to have a U tube of the type described under the subject of the ethylene electrode. The electrolyte used in this experiment was $N/5$ sodium hydroxide. The oxygen used in the oxidation experiment was obtained by the electrolysis of barium hydroxide. The electrodes consisted of two platinum electrodes of the same type as used in the hydrogen electrode work, one in each arm of the U tube. Oxygen was allowed to bubble against one of the electrodes, and the electromotive force of this element was, therefore, that of a concentration element in which the oxygen on one side is about five times as concentrated as on the other. The concentration pole was positive.

Time	E. M. F.
12.02	0.0305
12.03	0.0300
12.04	0.0298

The above table shows that the E. M. F. for the system is practically constant. The study of the oxidation is now ready. One drop of a forty percent solution of formaldehyde is added to the sodium hydroxide solution on the side opposite to the one into which oxygen is bubbling. The value for the electromotive force immediately increased and reached a constant value.

Time	E. M. F.	Time	E. M. F.
12.05	0.4740	12.09	*0.4472*
12.07	0.4575	12.10	*0.4480*
12.08	*0.4500*	12.12	*0.4499*

Three drops more of formaldehyde were added and an additional increase of the E. M. F. was observed.

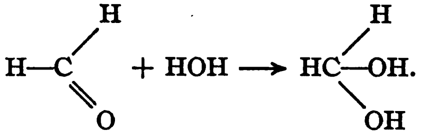
Time	E. M. F.
12.15	0.5270
12.17	0.5240

At this point air and carbon dioxide were blown through the solution, so that an idea of what effect blowing the formaldehyde out of the pipette had on the electromotive force. The reading dropped off to 0.505, showing that the result was not very large.

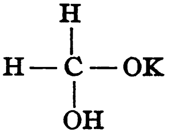
Theory of the reaction:

$$HCHO + O \longrightarrow HCOOH$$

It is well known that aldehydes are easily hydrated and possess acid properties.



In the presence of an alkali, NaOH or KOH, we would have the sodium or potassium salt formed as:

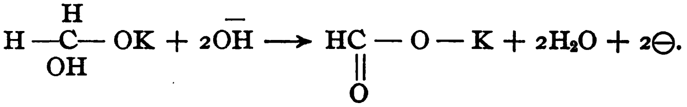


$$H-\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}-OK$$

When oxygen goes into solution at the anode, it reacts with HOH and takes up negative charges from the electrode for each atom of oxygen going over into the form

$$O \longrightarrow 2(\overline{OH}).$$

For every two $(\overline{OH})$ ions that go into solution, two $(\overline{OH})$ ions are discharged at the other pole in the reaction.

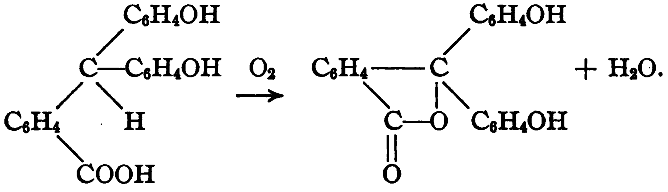
(A) 

$$H-\overset{H}{\underset{OH}{C}}-OK + 2\overline{OH} \longrightarrow H\underset{\underset{\large O}{\|}}{C}-O-K + 2H_2O + 2\ominus.$$

We do not attempt at this time to give any details of the reaction.

The object of this investigation is to determine whether the anion or molecule, or both, of the salt A is oxidized, and to learn the real mechanism as completely as possible. Now that a constant E. M. F. can be obtained we shall begin these studies quantitatively.

On the Oxidation of Phenolphthalin to Phenolphthalein



A small quantity of the phenolphthalin was dissolved in fifth normal sodium hydroxide, a clear colorless solution resulting. A sufficient amount of this solution was placed in the U tube which has been previously described. The relation between the two electrodes in sodium hydroxide solution was found to be 0.03 volt, when oxygen was passed over one and air over the other. The electromotive force in the presence of the phenolphthalin solution gave a value of 0.176 volt, and no perceptible red or pink color appeared even though the two poles of the cell were connected. The solution was now electrolyzed with an E. M. F. of 4.4 volts and a red color appeared at the anode, a proof that the phenolphthalin is oxidized electrolytically to phenolphthalein. Believing that the reverse reaction might take place we tried the next experiment described under reduction.

Reduction of Phenolphthalein to Phenolphthalin

In one arm of the U tube a *N*/5 sodium hydroxide solution of phenolphthalein (red in color) was placed; in the other fifth normal sodium hydroxide. The platinum electrodes were adjusted and hydrogen was bubbled into the solution continuously. The E. M. F. recorded in this case was 0.845 volt. The color of the solution grew lighter.

These experiments, though qualitative, point out the significance of the study of the electromotive forces of reactions. It leads us to consider that some electronic changes are going on in reactions whether they are organic or inorganic, and these changes should be studied quantitatively.

Summary

These qualitative experiments indicate the extreme importance of the study of the electromotive force of chemical reactions, whether they may be of the oxidation or reduction type, or even reactions involving neutralization. It is hoped that these few qualitative experiments will serve as an incentive to more careful quantitative investigations of these chemical reactions from the point of view of the ion and the molecule and the electronic charges which they may carry.